

Phase behavior of β -D galactose pentaacetate–carbon dioxide binary system

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Abstract

Phase behavior of β -D galactose pentaacetate–carbon dioxide binary system is investigated by dew-point and bubble-point measurements conducted in a high pressure variable volume sapphire cell. The phase envelope for solutions of β -D galactose pentaacetate in supercritical CO_2 is obtained for β -D galactose pentaacetate concentrations between 2 and 26 wt%, and for the temperature range of 308–323 K. The system exhibits lower critical solution temperature (LCST) behavior and high solubility of β -D galactose pentaacetate is observed. The densities of the system are also measured, and liquid-like densities (near 1 g/cm^3) are observed for single-phase solutions of β -D galactose pentaacetate in supercritical CO_2 at concentrations of 18 wt% and higher. Viscosity is measured for solutions of 18 and 25 wt% β -D galactose pentaacetate in the single-phase region at 313 K and 17 MPa and the viscosity values, 0.095 and 0.103 cp, respectively, are similar in magnitude to the viscosity of pure carbon dioxide. © 2005 Elsevier B.V. All rights reserved.

Keywords: β -D Galactose pentaacetate; Sugar acetate; Supercritical carbon dioxide; Solubility; Phase equilibria

1. Introduction

The high costs of using organic solvents in manufacturing processes, and increasingly stringent environmental regulations drive the development of new technologies based on supercritical fluid solvents, to produce products and materials without emissions and waste. Compounds soluble in supercritical carbon dioxide have many potential uses in materials processing operations such as casting and molding, as CO_2 -extractable binders and templates. However, the selection of appropriate CO_2 -soluble materials for such applications is limited by the low solvent strength of CO_2 for polar and ionic compounds, and for most polymers. Certain polysiloxanes and fluorinated polymers are highly soluble in CO_2 , but their applications are limited by the fact that soluble polysiloxanes have a very low T_g , and are liquid at ambient temperature, and fluorinated polymers have high cost, limited availability and environmental restrictions [1–4]. Therefore, one of the main focuses of research in supercritical or near critical CO_2 materials processing is the

investigation of CO_2 -philic groups and their applications for increasing the solubility of easily available and environmentally benign compounds [5–8]. Recently, hydrocarbons substituted with carbonyl groups have been shown to be highly soluble in supercritical carbon dioxide. Ab initio calculations and IR spectroscopic studies indicate the Lewis acid–Lewis base interaction between CO_2 and the electron donating carbonyl groups as the reason for the high solubility of these carbonyl systems in carbon dioxide [8–10]. For example, solubility of silicones in CO_2 can be increased substantially by the addition of acetate side chains [11]. Another example of this interaction is observed in the relatively high solubility of poly(vinyl acetate) in CO_2 [12].

Sugar acetates, which are peracetylated derivatives of multi-hydroxylated saccharides, are another class of materials with the potential for high solubility in carbon dioxide. Solubility of some derivatives of these sugars with acetate functionalities in CO_2 has been investigated [12–15]. High solubility of acetylated molecules in CO_2 is attributed to the Lewis acid–Lewis base interaction between CO_2 and the carbonyl group. Weak but cooperative hydrogen bonding between hydrogen of the carbonyl group and the oxygen of CO_2 is the second reason for the enhanced solubility of these sugar acetates [10,14]. In this paper, the phase behavior of one of these sugar acetate deriva-

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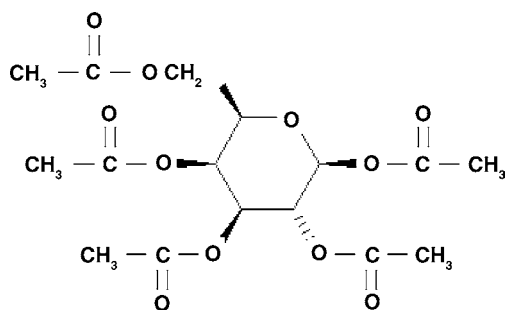


Fig. 1. Structural formula of β -D galactose pentaacetate.

tives, β -D galactose pentaacetate (Fig. 1) in supercritical CO_2 is investigated.

2. Experimental

2.1. Materials

β -D Galactose pentaacetate is obtained from Aldrich as 98% $\text{C}_{16}\text{H}_{22}\text{O}_{11}$, with a melting point 412–415 K. β -D Galactose pentaacetate is supplied in very fine powder form, but we find it convenient to solution cast the original sugar acetate powder in chloroform to produce thin plates of the compound for use in our experiments. Carbon dioxide is supplied by Airgas at 99.8% purity.

2.2. Experimental set-up

Dew and bubble points of β -D galactose pentaacetate– CO_2 mixtures are measured in a high pressure, variable volume sapphire cell enclosed in a cabinet-style air bath. A schematic diagram of the experimental set-up is given in Fig. 2. The same

type of apparatus has been used previously by other research groups for simultaneous determination of vapor–liquid equilibria and saturated densities of binary or ternary systems [16–18].

The main part of the apparatus is a 2.5 cm i.d. visible cell, with sample volume of about 60 cm^3 , containing a floating piston that separates the sample from a working fluid that controls the piston position, which is determined within $\pm 0.1\text{ mm}$ with a sighting telescope and a calibrated scale. The cell is loaded with CO_2 from a dip tube CO_2 cylinder, and the mass of CO_2 loaded is determined from the known temperature, pressure and volume, to within an estimated mass accuracy of 1.8%. The cell remains enclosed in the air bath for the duration of the experiment to maintain temperature control. Temperature and pressure of the sample fluid are measured by a thermocouple and pressure transducer mounted in the top cap of the cell. Temperature measurements are within an accuracy of $\pm 0.5\text{ K}$. The pressure of the working fluid under the piston is also measured during the operation. System was originally designed to measure pressure only on the working fluid side of the piston. However, piston friction can lead to significant pressure differences (up to 1 MPa) across the piston, so an Entran pressure transducer was installed to measure the sample pressure directly, with an accuracy of $\pm 0.5\%$.

A positive displacement pump supplies working fluid (an oil) to the visible cell to control the position of the piston and the sample volume. A needle valve was added to the working fluid line to control the decompression rate of the system during dew-point measurements. The needle valve allows us to perform decompressions at very slow rates, thereby avoiding measurement errors due to Joule–Thomson cooling of the sample during decompression. A magnetic stirrer is available on the sample side of the floating piston to speed up the dissolution of sugar acetate, and also to shorten the time necessary to reach equilibrium between phases.

2.3. Experimental procedure

Phase behavior of β -D galactose pentaacetate in CO_2 is obtained by two different types of measurements. Dew points are determined visually during volumetric decompression experiments, whereas bubble points are measured by determining the transition in overall system compressibility that accompanies the change from two phases to a single liquid phase during volumetric compression. Main difference between two techniques is the method of detecting the inception of a phase change. At the dew point, turbidity forms throughout the sample due to the formation of a second phase. Thus dew points can be readily and accurately determined by visual observation of the scattering of the laser sheet. In contrast, the first bubble of newly formed vapor during a bubble-point measurement may nucleate at an isolated location in the cell outside the range of visibility (e.g. inside a recession in the top cap, where lines enter the cell). Thus, the determination of the bubble point from the transition in system compressibility is more sensitive than a visual measurement.

A weighed amount of sugar acetate ($\pm 0.0001\text{ g}$) is loaded into the variable volume sapphire cell to achieve the desired concentration. After sealing and assembling, the cell is inserted in the

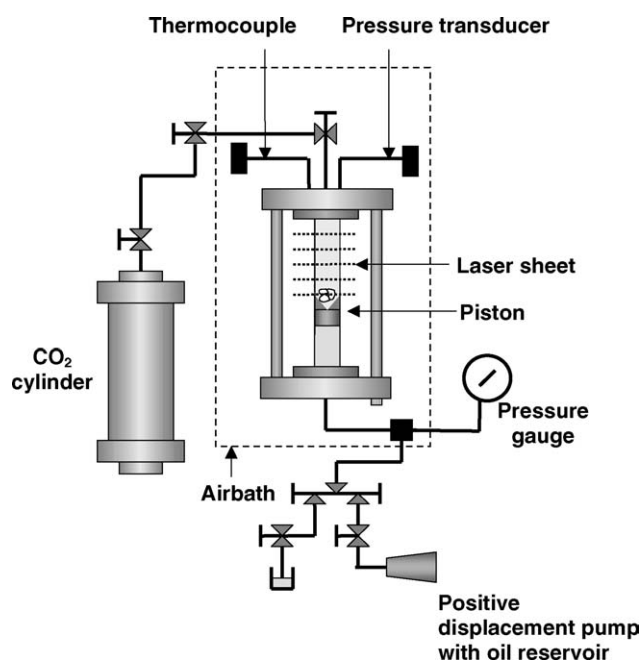


Fig. 2. High pressure variable volume sapphire cell.

air chamber. The cell and the connection line to the CO₂ tank are initially evacuated to eliminate air left inside the system. After evacuation, the volume of the cell loaded with sugar acetate is determined by pushing the piston to the bottom of the cell by injecting a very small amount of CO₂. At this point, pressure reaches about 0.3 MPa. This minimum height of the piston is recorded to obtain the maximum volume of the cell. The initial piston height reading changes for each run since the position indicator is reassembled for each new loading. After pushing the piston all the way to the bottom, a small amount of CO₂ is sent into the cell to reach a pressure around 0.8 MPa. At this condition, height of the piston, pressure and temperature of the system are recorded. Then the cell is isolated and compressed by increasing the piston's height. Pressure and temperature of the system and the height of the piston are recorded one more time. From the known PVT behavior of pure carbon dioxide at these conditions and the two positions of the piston, the volume of the cell that is filled with CO₂ is determined. The piston is then lowered, temperature is set at about 299 K, and the system is loaded with CO₂ gas at the cylinder pressure (about 7 MPa). Mass of CO₂ loaded into the cell is determined from the cell volume, measured pressure and temperature of the system, and the known density of carbon dioxide. The density of the pure CO₂ is determined by using the Reference Fluid Properties Software (REFPROP) produced by National Institute of Standards and Technology (NIST).

2.4. Dew-point measurements

Temperature for the phase behavior experiments is set after loading the high pressure sapphire cell, and the system is compressed to initiate the dissolution of the sugar acetate. During dissolution into CO₂, β -D galactose pentaacetate forms a sugar acetate-rich liquid phase swollen with CO₂. As dissolution continues, sugar acetate dissolves into the upper CO₂ rich phase. When all of the β -D galactose pentaacetate is dissolved in CO₂, the system is further compressed until a single-phase solution is obtained. Then the cell and the single-phase solution are allowed to reach the equilibrium pressure and temperature. When the system is stabilized, the needle valve connected to the working fluid line is opened slightly, allowing the sample to decompress. Decompression is kept at a slow and steady rate to avoid any possible temperature fluctuations due to the Joule–Thomson effect. Dew point is determined at the moment when turbidity caused by formation of a second phase is detected by scattering of the laser light sheet. This newly formed phase is a dense sugar acetate rich, lower phase. After pressure and temperature of the dew point are recorded, the system is pressurized again and equilibrated at the next desired temperature to get the dew point at new conditions for the same composition. Thus, the dew points are measured at all desired temperatures for that specific composition.

2.5. Bubble-point measurements

Bubble points are determined by compression of a two-phase system step by step until a phase transition occurs, and the system becomes single phase. At the bubble point, there is discontinu-

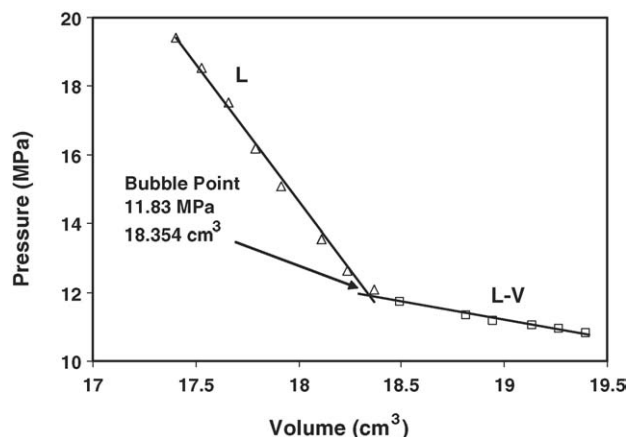


Fig. 3. A typical pressure–volume plot for a bubble-point measurement of 21 wt% β -D galactose pentaacetate system at 313 K.

ity in the slope of the pressure–volume curve, due to a change in system compressibility upon formation of a single-phase liquid. The cell loading procedure described above is also followed for bubble-point measurements. When the sugar acetate is completely dissolved in supercritical carbon dioxide and the system reaches a single phase, it is decompressed into the two-phase region, where the system consists of liquid and vapor in equilibrium with each other separated by a meniscus. The system is then compressed step by step, in small volume increments. After each compression, the system is stirred and allowed to equilibrate. The compression is continued until the system reaches the single-phase region, where the meniscus between the phases disappears. The bubble point is determined by plotting the volume of the system versus pressure. Two different lines with different slopes are obtained from this plot, as shown in Fig. 3. The intersection of these lines, where a discontinuity in system compressibility signals a phase transition, yields the bubble point.

3. Results and discussion

The phase envelope for β -D galactose pentaacetate–CO₂ binary system is obtained for overall concentrations between 2 and 26 wt% β -D galactose pentaacetate, and for the temperature and pressure ranges of 308–323 K and 9–16 MPa. The dew-point and bubble-point measurements are listed in Table 1. The first part of the phase envelope is obtained by dew-point measurements for the concentration range between 2 and 18 wt%. The dew points are displayed in Fig. 4. The area below each curve is the region where two phases exist, whereas a single-phase solution exists in the regions above the curves, representing complete solubility of the sugar acetate in carbon dioxide. The dew-point curves are linear and the slopes of dew-point curves increase with increasing sugar acetate concentration. At a constant β -D galactose pentaacetate concentration, pressure necessary to keep the sugar acetate solution in the single-phase region increases with the increasing temperature. Therefore, the system has the characteristics of lower critical solution temperature (LCST) phase behavior.

Table 1

Temperature and pressure data of dew and bubble points of β -D galactose pentaacetate–CO₂ binary system

SA wt fraction ($\pm 1.8\%$)	308 K		313 K		318 K		323 K	
	Pressure (MPa) ($\pm 0.5\%$)	Phase transition	Pressure (MPa) ($\pm 0.5\%$)	Phase transition	Pressure (MPa) ($\pm 0.5\%$)	Phase transition	Pressure (MPa) ($\pm 0.5\%$)	Phase transition
0.021	9.01	DP	10.35	DP	11.70	DP	13.03	DP
0.037	9.39	DP	10.89	DP	12.38	DP	13.88	DP
0.075	9.77	DP	11.48	DP	13.19	DP	14.90	DP
0.109	10.06	DP	11.79	DP	13.52	DP	15.26	DP
0.128	10.21	DP	11.97	DP	13.74	DP	15.49	DP
0.182	10.28	DP	12.09	DP	13.89	DP	15.69	DP
0.206	9.98	BP	11.82	BP	13.65	BP	15.49	BP
0.259	10.21	BP	11.50	BP	12.78	BP	14.07	BP

SA: sugar acetate, DP: dew point; BP: bubble point.

Reproducibility of the dew point detection method is confirmed by repeating decompressions from the single-phase region for several different sample loadings and temperatures. As shown in Fig. 4, the reproducibility of the dew-point measurements is very good. Reproduced dew points are indicated by solid symbols in Fig. 4. Note that slight temperature changes accompany the repeated dew points.

For β -D galactose pentaacetate concentrations above 18 wt%, the phase envelope is obtained by bubble-point measurements. These measurements are performed by volumetric compression as explained in Section 2. The overall phase envelope is obtained by combining the dew and bubble points. Dew and bubble points measured at four different temperatures in the range of 308–323 K are shown in Fig. 5, with trend lines represented by second order polynomial curves. Dew-point measurements, detection of the nucleation of a vapor phase by slowly decompressing a single-phase system, and bubble-point measurements, detection of the compressibility change as a two-phase system becomes a single-phase system, yield consistent measurements of the phase envelope. Each of these curves represents a phase boundary at a constant temperature separating a two-phase sys-

tem from a single-phase system. The region below each curve is a two-phase liquid–vapor region and above is the single-phase region. As observed in the dew-point measurements, the overall phase envelope has the characteristic of a lower critical solution temperature (LCST) system, since the pressure required to keep the system at single phase is increasing with increasing temperature. The maximum pressure required to dissolve β -D galactose pentaacetate at 308 K is 10.3 MPa (obtained for the concentration of 15 wt%) whereas this value reaches 15.7 MPa for 323 K. The same general type of overall phase behavior is also described by Hong et al. for the global phase behavior of CO₂–maltose octaacetate system over a wide range of pressure and composition at several temperatures [15].

CO₂ is a nonpolar solvent with a low dielectric constant and its solvent strength directly depends on its density, which is adjustable by changing temperature and pressure. Pure CO₂ densities, calculated by the REFPROP equation of state using the measured dew-point and bubble-point temperatures and pressures, are plotted against wt% of β -D galactose pentaacetate in Fig. 6. A master-curve is obtained for the solubility of β -D galactose pentaacetate in CO₂, when plotted against this mea-

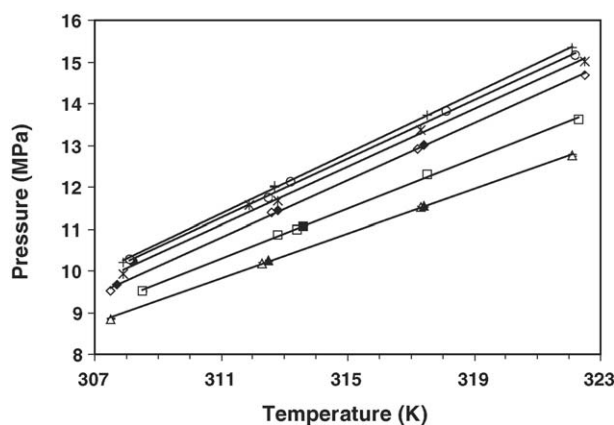


Fig. 4. Dew-point curves at various compositions of β -D galactose pentaacetate: (Δ) 2.1 wt%; (\square) 3.7 wt%; (\diamond) 7.5 wt%; (\times) 10.9 wt%; (\circ) 12.8 wt%; (+) 18.2 wt%; solid lines are trendlines. Solid points (\bullet), (\blacklozenge), (\blacksquare), (\blacktriangle) are the reproduced dew-point measurements for those compositions (see text). Errors in dew-point measurements are comparable to the size of the symbols used in this plot.

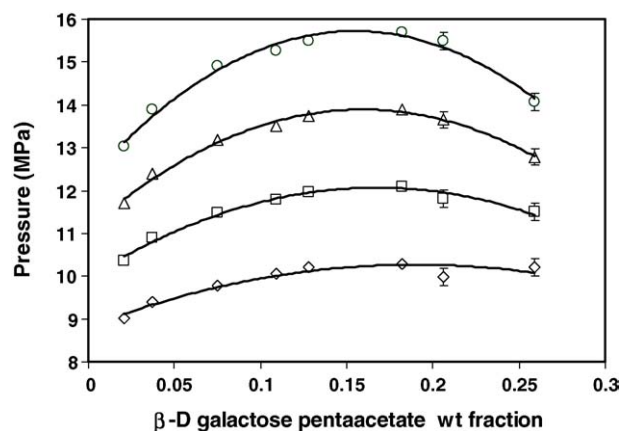


Fig. 5. Pressure-concentration plot of β -D galactose pentaacetate–CO₂ system phase envelopes at (\diamond) 308 K; (\square) 313 K; (Δ) 318 K; (\circ) 323 K. Solid lines are trendlines. Estimated error bars are shown for bubble-point measurements. For the remaining points, which are dew points, the error bars are comparable to the size of the symbols.

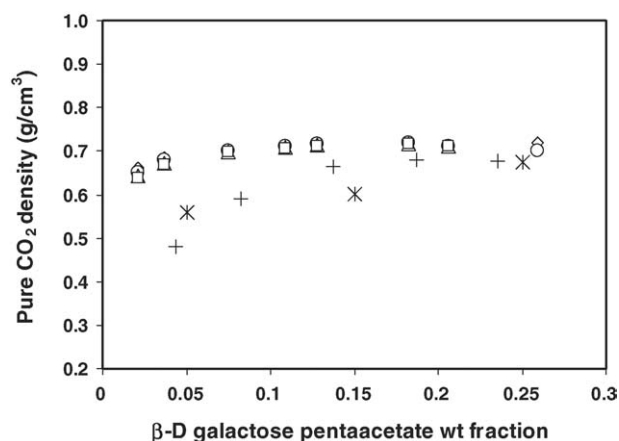


Fig. 6. Density of the pure CO₂ at temperatures and pressures corresponding to points along the phase envelopes for β-D galactose pentaacetate–CO₂ solutions and comparison of the data with the previous studies; (◇) this study at 308 K; (○) this study at 313 K; (△) this study at 318 K; (□) this study at 323 K; (X) Potluri et al. [12] at 313 K; (+) Raveendran and Wallen [10] at 313 K.

sure of solvent strength. The solubility curve is relatively flat indicative of highly soluble solutes in minimally selective solvents. 10–25 wt% of β-D galactose pentaacetate is soluble in CO₂ once the CO₂ density exceeds 0.7 g/cm³. In Fig. 6, pure CO₂ densities, calculated similarly from the temperatures and pressures of points along the phase envelopes as reported in previous studies, are also plotted. There is good agreement between our results and the previous studies in the higher concentration range, but some deviations at lower concentrations. We surmise that our results are more accurate than previous literature values, because we perform direct measurements of pressure in the sample compartment whereas the previous results report dew-point pressures that do not take into account the pressure difference due to piston friction. This potential source of error is expected to be more serious at low dew-point pressures, which correspond to the low concentration region in Fig. 6, where deviations are greatest.

In the single-phase region, density can be easily obtained by dividing the known combined weight of carbon dioxide and β-D galactose pentaacetate by the sample volume, calculated from the position of the piston. When the overall system densities are investigated at the measured dew and bubble points, an increase in the system density is observed with increasing concentration of β-D galactose pentaacetate, as shown in Fig. 7. Binary system densities obtained at dew points increase from 0.70 to 1.0 g/cm³ as β-D galactose pentaacetate composition increases from 2 to 18 wt%. These densities represent the saturated vapor densities of the binary system. The densities measured at bubble points for the higher concentration region, representing the densities of saturated liquids, are about 1.0 g/cm³ for β-D galactose pentaacetate composition greater than 18 wt%.

Bubble-point measurements also yield density measurements for single-phase liquids at points along the liquid compression curve illustrated in Fig. 3. These liquid density values are listed in Table 2.

In many potential applications, transport properties of the sugar acetate liquid phase may be of importance. In demon-

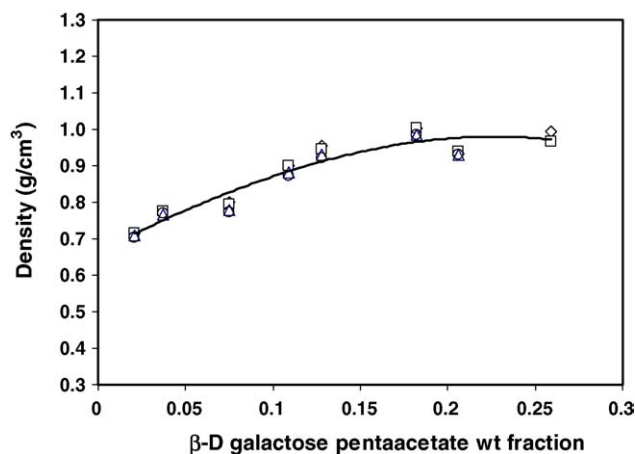


Fig. 7. Density of saturated β-D galactose pentaacetate–CO₂ binary systems measured at dew points and bubble points between 308 and 323 K; (◇) 308 K; (□) 313 K; (△) 318 K; (○) 323 K. Solid line is the trendline for the data points.

Table 2
Measured liquid densities

β-D Galactose pentaacetate wt fraction	Temperature (K)	Pressure (MPa)	Density (g/cm ³) ±2%
0.206	308	10.6	0.93
0.206	308	11.4	0.94
0.206	308	12.3	0.95
0.206	308	13.7	0.96
0.206	308	15.0	0.97
0.206	308	15.5	0.97
0.206	313	12.1	0.94
0.206	313	12.7	0.94
0.206	313	13.6	0.95
0.206	313	15.1	0.96
0.206	313	16.2	0.97
0.206	313	17.5	0.98
0.206	313	18.5	0.98
0.206	313	19.4	0.98
0.206	318	14.4	0.93
0.206	318	15.1	0.94
0.206	318	15.9	0.94
0.206	318	16.7	0.95
0.206	318	17.9	0.96
0.206	318	20.3	0.97
0.206	323	15.5	0.93
0.206	323	16.0	0.94
0.206	323	16.6	0.94
0.206	323	17.7	0.95
0.206	323	18.9	0.96
0.259	308	10.6	0.99
0.259	308	11.0	1.00
0.259	308	11.7	1.01
0.259	308	12.4	1.02
0.259	308	13.3	1.03
0.259	308	14.9	1.04
0.259	308	17.1	1.06
0.259	313	11.9	0.97
0.259	313	12.6	0.98
0.259	313	13.3	0.98
0.259	313	14.2	0.99
0.259	313	15.1	1.00
0.259	313	15.8	1.01
0.259	313	17.3	1.02
0.259	313	19.8	1.04

Table 3

Viscosities of pure CO₂, 18 wt% β-D galactose pentaacetate and 25 wt% β-D galactose pentaacetate solutions at 40 °C and 17 MPa

318 K, 17 MPa	Viscosity (cp)
Pure carbon dioxide	0.074
18 wt% β-D galactose pentaacetate	0.095
25 wt% β-D galactose pentaacetate	0.103

stration experiments designed to study sugar acetate dissolution rates, we observe the formation of a transient CO₂ swollen liquid phase. Gravity drainage of this liquid phase appears to contribute significantly to the rate of dissolution of sugar acetate. In such extraction processes, the rate of gravity drainage of sugar acetate extracted as a CO₂ swollen liquid will depend on viscosity. Here, the viscosity of the binary system in the single-phase region is measured with a high pressure falling cylinder viscometer. The experimental set-up and the procedure is described by Shi et al. [19]. Viscosity of β-D galactose pentaacetate in supercritical CO₂ is measured at 17 MPa and 313 K for concentrations 18 and 25 wt%. Viscosities are determined from the terminal velocity of the cylinder in a single-phase binary system using Eq. (1), where K is the calibration constant for the cylinder, u_t the terminal velocity of the falling cylinder, ρ_s the solid cylinder density, ρ_l the fluid density and η_f is the fluid viscosity. The calibration constant was determined from the terminal velocity of the cylinder in pure carbon dioxide at the same temperature and pressure as the binary system viscosity measurements:

$$\eta_f = \frac{K(\rho_s - \rho_l)}{u_t} \quad (1)$$

Measured viscosities are given in Table 3. Overall, these results show that although the binary system reaches liquid-like densities with high concentrations of β-D galactose pentaacetate, the viscosity remains similar to that of pure supercritical CO₂. Viscosity of the single-phase binary system does not appear to depend strongly on the concentration of β-D galactose pentaacetate.

4. Conclusions

The phase behavior of β-D galactose pentaacetate and supercritical CO₂ binary system is investigated by dew-point and bubble-point measurements conducted in a high pressure, variable volume sapphire cell. β-D Galactose pentaacetate has substantial solubility in CO₂ and exhibits a lower critical solution temperature (LCST) type phase behavior. The phase envelope is obtained in the temperature range 308–323 K for the concentration range of 2–26 wt%. Dew-point measurements are employed below 18 wt% sugar acetate and bubble-point measurements

are employed at higher concentrations to determine the full phase envelope. Solutions with high concentrations (>18 wt%) of β-D galactose pentaacetate in CO₂ exhibit liquid-like density (~1g/cm³) in the single-phase regions, while the corresponding viscosities are close to that of pure CO₂.

List of symbols

K	calibration constant for the cylinder
u_t	terminal velocity of the falling cylinder
ρ_s	solid cylinder density
ρ_l	fluid density
η_f	fluid viscosity

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